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Current- and past-use pesticide prevalence in drainage ditches in the Lower Mississippi Alluvial Valley

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Abstract

BACKGROUND: Pesticide application is common in agriculture and often results in applied pesticides entering adjacent aquatic systems. This study seasonally analyzed a suite of 17 current- and past-use pesticides in both drainage waters and sediments to evaluate the prevalence of pesticides in drainage ditches across the Lower Mississippi Alluvial Valley (LMAV).

RESULTS: There were significantly higher concentrations ($P < 0.05$) of current-use than past-use pesticides; however, there were consistently high numbers of detections of past-use pesticides in sediments. Sediment pesticide concentrations were an order of magnitude higher (150–1035 μg kg^{-1}) than water samples (6–20.9 μg L^{-1}). Overall, 87% of all samples analyzed for current- and past-use pesticides were non-detects. *p,p′*-DDT was detected in 47.5% of all drainage waters and sediments sampled. There were significant correlations ($0.372 \geq r^2 \leq 0.935$) between detected current-use water and sediment concentrations, but no significant correlations between past-use water and sediment concentrations.

CONCLUSION: Overall, there was a high percentage (87%) of sediment and water samples that did not contain detectable concentrations above the lower limit of analytical detection for each respective pesticide. This lack of pesticide prevalence highlights the improved conditions in aquatic systems adjacent to agriculture and a potential decrease in toxicity associated with pesticides in agricultural landscapes in the LMAV.

Keywords: drainage ditch; LMAV; pesticide; prevalence; DDT

1 INTRODUCTION

The Lower Mississippi Alluvial Valley (LMAV) is one of the most productive agricultural areas in the conterminous United States. According to the US Department of Agriculture's National Agricultural Statistics Service (USDA-NASS), the states of Mississippi, Arkansas and Louisiana contain approximately 6 256 900 ha of principal crops, including cotton, rice, soybeans and corn.[1] Use of fertilizers and pesticides help to achieve this high-level agricultural production. Pesticide use increased 40-fold from 1946 to 1976 and continues to be necessary to maintain food and fiber production for a growing global population.[2,3] While 546 800 000 kg of pesticide active ingredient was applied to the US landscape in 2001, nearly 2 294 000 000 kg was applied globally in the same year.[4]

A number of pesticide classes are concomitant with the agricultural region of the LMAV. Herbicides such as atrazine, alachlor and metolachlor are still in current use, while insecticides have undergone several class changes. Older classes of persistent pesticides, such as organochlorines, were phased out and replaced with a less persistent class of pesticide known as organophosphates. Today, organophosphates are being phased out in favor of synthetic pyrethroid insecticides. Pimentel *et al.*[5] noted that, since 1972, there has been little change in the amount of pesticides (i.e. mass) being applied. The change has instead been in the use of pesticides with a higher level of toxicity and a shorter environmental half-life.[5] Within the Mississippi Delta, some intensively agricultural areas have received pesticide applications for over 150 years.[6] Because of the region's historical and continued intensive use of agrochemicals, it is not uncommon to detect pesticides in surface water or sediments of drainage systems, rivers or lakes. Even organochlorines, such as DDT, banned in the early 1970s, are still detected in samples collected throughout the LMAV.[7,8] Several studies have examined groundwater samples within agricultural areas, and focused studies have also been conducted on pesticide contamination of surface water in aquatic receiving systems.[4–6] Few studies, however, have examined the prevalence of current- and past-use pesticides in drainage systems associated with agriculture. These drainage systems are often the site of first contact for runoff before it is transported to an aquatic receiving system, such as a lake, river or stream.

Agricultural drainage ditches are commonplace within the production landscape of the LMAV. Historically, ditches were

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viewed as little more than conduits for the rapid removal of water from cropland following storm events. Research within the last decade, however, has demonstrated the ability of these systems to filter contaminants from runoff water.[6,9,10] Because ditches intercept agricultural runoff and can act as filters, it is reasonable to assume that they would reflect variable concentrations of pesticides, based on half-life degradation rates, from within ditch applications as well as surface-runoff-driven applications from respective drainage areas. Past-use pesticides with prolonged half-lives should also be measurable in these drainage systems (primarily in sediments), based on initial contact and adsorption with surface runoff, with temporal correlations probable during times of increased runoff and sediment delivery.

The objective of this study was to measure the prevalence of selected current- and past-use pesticides in drainage ditch waters and sediments associated with row-crop agriculture in the LMAV. A complete assessment of every possible applied pesticide would be fiscally impossible and time consuming, given that the sample locations encompassed four states. Therefore, a suite of 17 pesticides (Table 1) were targeted because of their common use in the LMAV.[6] Current-use pesticides were defined as pesticides in common use today in agriculture within the LMAV. This included commonly used pesticides such as atrazine (corn), methyl parathion (cotton) and metolachlor (corn, soybeans). Past-use pesticides and derivative metabolites of particular interest were those that had been banned: *p,p′*-DDT, DDE, DDD and dieldrin. Current-use pesticides not analyzed for included imidacloprid, 2,4-D, diazinon (phasing out), fipronil-sulfide and desulfinyl, and *cis-trans* permethrin. By examining pesticide prevalence in ditch water and sediment, a better assessment of long-term contamination of these systems can be achieved. This is important for understanding how ditch systems potentially transport pesticides in runoff.

2 EXPERIMENTAL METHODS

2.1 Sampling design

Drainage ditch sediments were collected on four quarterly sampling events throughout 2008 (January, March/April, June and September). Seven drainage ditch sites throughout the LMAV (Fig. 1) and a single ditch site outside the LMAV (Oxford, MS) were sampled to understand the prevalence of pesticides, *in situ*, in drainage ditches associated with row-crop agriculture (Table 1). Drainage ditch width (<2.1–9.9 m) and length (57–1092 m) varied between and within sites. All drainage sites were cropped in either corn, soybeans, cotton or rice, the four predominant agricultural crops in the LMAV. Three ditches were sampled at each site during each quarterly sampling event. Within each ditch, three sediment and water samples were taken along the longitudinal gradient of the drainage ditch. This provided a total of 261 drainage sediments and 210 water samples (lower sample number due to dry conditions at some sites throughout the year). Sediment samples (±1 kg of sediment) were taken from the upper 15 cm of the soil profile in the middle of each drainage channel using a shovel and were homogenized within a zip-sealed plastic bag (transferred to aluminum foil for drying). Water samples were taken prior to sediment collection in 1 L wide-mouth amber glass bottles to avoid unintentional suspended sediment inclusion. Sediment and water samples were labeled accordingly, and transported on ice from the field to the USDA-Agricultural Research Service National Sedimentation Laboratory in Oxford, MS, for pesticide analysis.

2.2 Pesticide analyses

In the laboratory, 500 mL water samples were fixed with 500 mg of KCl and 100 mL of distilled ethyl acetate and prepared within 48 h for analysis.[7,8] Sediment samples were frozen, air dried in a greenhouse to constant weight and ground with a Wiley mill prior to pesticide analysis.[7,8,11] A quantity of 5 g of sediment was used in pesticide extraction analysis. Further details on sample preparation and extraction techniques can be found in Bennett *et al.*,[11] Smith and Cooper[8] and Smith *et al.*[7] Sediment and water analytes were analyzed by gas chromatography–electron capture detection (GC-ECD) using an HP model 6890 gas chromotagraph equipped with dual HP 7683 ALS autoinjectors, dual split-splitless inlets, dual capillary columns, a HP Kayak XA chemstation[12] and a main 30 m × 0.25 mm ID (0.25 µm film thickness) HP 5 MS capillary column. Two Agilent electron capture detectors analyzed analytes at 325 °C with UHP nitrogen make-up gas. A suite of 17 pesticides were analyzed on the HP 5 MS column for a single run through the GC. Table 2 includes data on each pesticide analyzed and minimum detection limits (MDLs), as well as pesticide type and mean derived K_{oc} from literature sources. The MDL for the 17-pesticide GC run was determined using external standards for the 17 pesticides (AccuStandard® 17p1 and 17p2), conducting quality-controlled replicates ($n = 30$) at 1 ppm and diluting samples 1 : 10 for determination of detection limits for 500 mL ($n = 30$), as well as 1 : 20 ($n = 30$) and 1 : 100 ($n = 30$) dilutions on 1 ppm solutions. Recoveries within 20% of the expected concentration due to dilution were averaged to determine detection limits. The MDL in this analysis is the practical quantitation limit (PQL), as the concentrations determined at minimum detections were actual limits of precision and accuracy during routine laboratory operating conditions. Quality assurance and quality control (QC) methods for pesticide runs included a bracketed, triplicate-level calibration standard curve for all 17 pesticides around the expected sample concentration. Recovery percentages were upwards of 95% recovery for every tenth sample (middle standard) delivered. Blanks (reagent-grade ethyl acetate) were paired with matrix spikes to limit noise in sample pesticide recovery. Known standards, different from calibration standards, were used for QC checks every 20 samples throughout the GC run. Pesticide recovery for each external standard was greater than 95%, and occasional and random duplicates (90–110% relative percentage difference) were utilized to assure accuracy of lab techniques.

2.3 Statistical analyses

The low overall percentage of detection between sites and sampling events precluded high replicated comparisons between sites. Data comparisons of samples above the MDL were log transformed to meet parametric assumptions of normality, and analyzed using a one-way ANOVA to provide site-wise comparisons of pesticide concentrations between sites.[12] Only detected concentrations above the MDL were compared. Individual Pearson's linear correlations were performed for each pesticide concentration above the MDL in water and sediment by site, and to test for trends between water and sediment concentration and average K_{oc} values. No statistically powerful seasonal correlations could be made with the detected water and sediment samples, as the number of detections by sampling date for each pesticide was very low. The K_{oc} values were accumulated from various literature sources (see Supplementary material A) and Extoxnet,[13] with a mean K_{oc} value derived for each pesticide.

Table 1. Physical and landscape characteristics of sample sites within the Lower Mississippi Alluvial Valley

Site name	Latitude (N)	Longitude (W)	Ditch depth (m)[a]	Ditch width (m)[a]	Ditch length (m)[b]	Area drained (ha)	Crop type	Water presence/ depth
Beasley	33° 23.401′	90° 40.931′	2.1 ± 1	7.9 ± 2.8	630	90	Soybeans	Wet,
					381	36		10–35 cm
					1092	235		
Jonesboro	35° 50.211′	90° 40.011′	0.4 ± 0.02	2.1 ± 0.01	57	5	Corn	Wet,
					58	4		5–15 cm
					60	4		
Judd Hill	35° 35.644′	90° 31.185′	0.8 ± 0.5	3.1 ± 1.7	778	56	Cotton	Dry, bar one sample
					591	64		
					768	54		
Oxford	34° 21.002′	89° 39.256′	1.8 ± 2.2	6.5 ± 0.5	126	4	Cotton	Wet,
					380	11		10–25 cm
					207	14		
Memphis	35° 08.121′	89° 49.458′	1.4 ± 0.8	4.5 ± 2.2	218	11	Corn	Wet,
					409	15		10–25 cm
					428	16		
Portageville	36° 23.754′	89° 36.379′	2.0 ± 0.6	7.4 ± 1.2	799	15	Cotton and corn	Typically dry,
					703	40		10–15 cm
					390	17		
Success	36° 26.108′	90° 45.448′	1.8 ± 1.6	5.7 ± 4	523	54	Rice	Inundated,
					593	29		∼5–8 cm
					250	69		
Tallahatchie County	33° 48.975′	90° 09.777′	3.8 ± 0.5	9.9 ± 1.9	653	80	Soybeans and corn	Present,
					335	48		∼5–8 cm
					890	70		

[a] Ditch depth and width was measured at three locations within each drainage ditch, at three different ditches per site (n = 9)
[b] Ditch length ($n = 3$).

3 RESULTS

3.1 Site-specific pesticide prevalence

The summary statistics, number and percentage detection for all 17 pesticides in both water and sediment samples for each site sampled are summarized in Tables 3 to 6. Detections for all 17 pesticides were very low in all drainage water samples ($16.33 \pm 8.2\%$). Similarly, detection of all 17 pesticides in sediments was also low ($10.7 \pm 8.5\%$). Atrazine had the highest concentration in both water ($20.9 \pm 18.5\ \mu g\ L^{-1}$) and sediment ($372 \pm 442\ \mu g\ kg^{-1}$) samples from Portageville, MO (Table 5). The overall detection for atrazine in water for Portageville was 70%, but this was 100% during the spring sampling period, with an average of $29.78 \pm 20.48\ \mu g\ L^{-1}$. The Beasley, MS site had similarly high sediment atrazine concentrations ($203 \pm 42\ \mu g\ kg^{-1}$), but low detection and concentrations in the water column ($1.49 \pm 6\ \mu g\ L^{-1}$; 13%). Similarly, metolachlor had high water ($5.4 \pm 13\ \mu g\ L^{-1}$) and sediment ($34.4 \pm 20\ \mu g\ kg^{-1}$) concentrations at Portageville, with 100% detection in water samples over the spring ($14.65 \pm 23\ \mu g\ L^{-1}$).

The Jonesboro, AR and Memphis, TN sites were the most urban sites with the least agricultural influence (Table 3). In Memphis water samples, all but two pesticides (lambda cyhalothrin and methyl parathion) were consistently detected; however, most of the detections were within 10% of the MDL. Atrazine was never detected in either water or sediment samples at Jonesboro, but was detected in 34% of all water samples from Memphis, often at high concentrations ($25.5 \pm 50\ \mu g\ L^{-1}$; max. $131\ \mu g\ L^{-1}$). Similar to Portageville, Memphis had 100% detection of atrazine in spring samples collected, with the highest average concentrations occurring over that sampling period ($33.3 \pm 57\ \mu g\ L^{-1}$).

p,p′-DDT concentrations were very low in drainage waters in the LMAV, with average concentrations of only $0.4 \pm 0.07\ \mu g\ L^{-1}$, which was only $0.2\ \mu g\ L^{-1}$ above the MDL for the analytical instrument. However, the average concentration in sediments was more than double the MDL ($45 \pm 36\ \mu g\ kg^{-1}$). Highest detected water *p,p*′-DDT concentrations were at Portageville, MO, with $1.2\ \mu g\ L^{-1}$, and $582\ \mu g\ kg^{-1}$ was the highest sediment *p,p*′-DDT concentration at Beasley, MS. Beasley and Tallahatchie County sites had measureable concentrations of *p,p*′-DDT, DDD and DDE in all water and sediment samples consistently throughout the sampling period. The average percentage detection for both water and sediment for both sites was 47.5%, almost 30% higher than the overall detection average. Comparing Portageville (corn) with Success, AR (rice), there were discernable differences in the number of pesticides detected in water (19.7 versus 10%) and sediment (21.3 versus 2.7%) and a lack of atrazine detections within sediments of Success. Comparing the Portageville and Success sites with other sites, there were much lower detections and average concentrations of *p,p*′-DDT, DDD and DDE. Judd Hill, AR, was often dry when sampled for water, but, when water samples

Figure 1. Distribution of drainage ditch sites within the Lower Mississippi Alluvial Valley.

were present, 75% of samples had detectable concentrations of *p,p′*-DDT (0.55 ± 3.9 µg L^{-1}), DDD (0.02 ± 0.007 µg L^{-1}) and DDE (0.029 ± 0.006 µg L^{-1}), although most were within 10% of the MDL.

3.2 Cumulative pesticide prevalence

Sediment samples had low overall average concentrations of pesticides (43.9 ± 13 µg kg^{-1}), with detectable average concentrations of metolachlor (50.2 µg kg^{-1}), methyl parathion (214 µg kg^{-1}), cyanazine (68 µg kg^{-1}) and *p,p′*-DDT (53 µg kg^{-1}). There were no significant correlations between detected water and sediment concentrations and season-sampled concentrations owing to the low sample size available. There were no statistically significant correlations between detected pesticides in soil and water and respective average soil absorption coefficients (K_{oc}) for each pesticide ($0.005 \geq r^2 \leq 0.01$), although these data were not normalized by respective TOC concentrations. There were significant ($P < 0.05$) correlations between current-use pesticide concentrations in water and sediment samples ($0.372 \geq r^2 \leq 0.935$). Atrazine had the highest correlation (0.9349), followed by trifluralin (0.745) and alachlor (0.567). There were no statistically significant correlations between water and sediment concentrations for *p,p′*-DDT, DDE and DDD ($0.0006 \geq r^2 \leq 0.118$), with no sample pairs above MDL for dieldrin.

Banned-use pesticides such as *p,p′*-DDT, DDE, DDD and dieldrin were typically absent from water and sediment samples (<36%) (Tables 3 to 6). When *p,p′*-DDT was detected, average concentrations were low or negligible (Table 7), as concentrations were close to the MDL (Table 1) for the analytical instrument (0.4 ± 0.01 µg L^{-1} water; 45.1 ± 36 µg kg^{-1} sediment). When detected, *p,p′*-DDE, DDD and dieldrin were all close to the lower limit of detection for both drainage water and drainage sediment

Table 2. Suite of pesticides analyzed for on a single GC run at the National Sedimentation Laboratory, Oxford, Mississippi (Smith *et al.*[7]). K_{oc} ranges came from Extoxnet and an extensive literature search (41 references)

Pesticide	Minimum detection limit[a] (µg L^{-1}) water	Minimum detection limit[a] (µg kg^{-1}) sediment	Type	$K_{oc/w}$[b]
Trifluralin	0.02	2	Herbicide	3750–13 000
Atrazine	1	100	Herbicide	61–274
Methyl parathion	2	200	Organophosphate	476–8912
Alachlor	0.1	10	Herbicide	120–412
Metolachlor	0.1	10	Herbicide	200–325
Chlorpyrifos	0.01	1	Organophosphate	4788–31 000
Cyanazine	0.1	10	Herbicide	73–413
Pendimethalin	0.05	5	Herbicide	13 000–24 547
Fipronil	0.2	20	Phenyl-pyrazole	749–825
Dieldrin[c]	0.02	2	Chlorinated hydrocarbon	10 593–54 300
p,p′-DDE[d]	0.02	2	Stable metabolite of DDT	50 118–1 000 000
Fipronil sulfone	0.02	2	Phenyl-pyrazole metabolite	1447–6745
Chlorfenapyr	0.02	2	Pyrrole insecticide	12 000–67 670
p,p′-DDD[d]	0.02	2	Stable metabolite of DDT	43 651–81 283
p,p′-DDT[d]	0.2	20	Organochlorine insecticide	100 000–1 819 700
Bifenthrin	0.02	2	Pyrethroid	72 444–4 265 795
Lambda-cyhalothrin	0.2	20	Pyrethroid	180 000–316 227

[a] MDL is equivalent to practical quantitation limit (PQL).
[b] *Extoxnet*. [Online]. National Pesticide Information Center, Oregon State University. Available: extoxnet.orst/edu/ghindex.html [21 April 2011].
[c] Banned 1985.
[d] Banned 1972.

Table 3. Summary statistics for both water and sediment samples above the minimum detection limit for each respective pesticide analyzed. Jonesboro and Memphis county site summary statistics are presented herein

		Jonesboro					Memphis				
		Overall ($\mu g\ L^{-1}$)					Overall ($\mu g\ L^{-1}$)				
Pesticide	MDL ($\mu g\ L^{-1}$)	Mean ± SD	Median	Min.	Max.	Number of detections (%)	Mean ± SD	Median	Min.	Max.	Number of detections (%)
Water											
Trifluralin	0.02	0.02 ± 0.003	0.028	0.024	0.032	3 (9)	0.03 ± 0.006	0.032	0.026	0.042	5 (16)
Atrazine	1	–	–	–	–	– (0)	25.5 ± 50	3.69	1.00	131	11 (34)
Methyl parathion	2	–	–	–	–	– (0)	–	–	–	–	– (0)
Alachlor	0.1	–	–	–	–	– (0)	0.27 ± 0.28	0.115	0.109	0.603	3 (9)
Metolachlor	0.1	–	–	–	–	– (0)	6.96 ± 17	0.251	0.116	52.1	15 (47)
Chlorpyrifos	0.01	–	–	–	–	– (0)	0.022	0.02	0.02	0.02	1 (3)
Cyanazine	0.1	–	–	–	–	– (0)	0.131 ± 0.025	0.145	0.102	0.148	3 (9)
Pendimethalin	0.05	–	–	–	–	– (0)	0.088 ± 0.04	0.065	0.058	0.143	3 (9)
Fipronil	0.2	–	–	–	–	– (0)	0.408 ± 0.24	0.408	0.234	0.582	2 (6)
Dieldrin[a]	0.02	–	–	–	–	– (0)	0.039 ± 0.025	0.033	0.02	0.096	7 (22)
p,p′-DDE[b]	0.02	–	–	–	–	– (0)	0.039 ± 0.014	0.04	0.02	0.058	6 (19)
Fipronil sulfone	0.02	0.021	0.02	0.02	0.02	1 (3)	0.04 ± 0.02	0.028	0.02	0.079	17 (53)
Chlorfenapyr	0.02	0.023 ± 0.007	0.023	0.023	0.024	2 (6)	0.034 ± 0.011	0.031	0.02	0.064	13 (40)
p,p′-DDD[b]	0.02	0.021	0.02	0.02	0.02	1 (3)	0.034 ± 0.008	0.034	0.021	0.047	12 (38)
p,p′-DDT[b]	0.2	0.342 ± 0.08	0.373	0.225	0.431	11 (32)	0.43 ± 0.34	0.316	0.202	1.16	7 (22)
Bifenthrin	0.02	–	–	–	–	– (0)	0.09 ± 0.06	0.085	0.025	0.169	4 (13)
Lambda-cyhalothrin	0.2	–	–	–	–	– (0)	–	–	–	–	– (0)
Overall site detection for all pesticides						3.1					20
Sediment											
Trifluralin	2	2.08	2.08	2.08	2.08	1(3)	2.5 ± 0.63	2.53	2.07	2.97	2 (6)
Atrazine	100	–	–	–	–	– (0)	–	–	–	–	– (0)
Methyl parathion	200	–	–	–	–	– (0)	–	–	–	–	– (0)
Alachlor	10	11.2 ± 1.3	11.2	10.3	12.2	2(6)	15.3	15	15	15	1 (3)
Metolachlor	10	14.1	14.1	14.1	14.1	1(3)	16.8 ± 6	13.4	13.1	23.7	3 (8)
Chlorpyrifos	1	1.2 ± 0.33	1.286	1.05	1.53	2(6)	2.35 ± 2.86	1.472	1.01	8.9	8 (22)
Cyanazine	10	11.07	11	11	11	1(3)	13.6	13.6	13.6	13.6	1 (3)
Pendimethalin	5	–	–	–	–	– (0)	5.89 ± 0.95	5.89	5.2	6.5	2 (6)
Fipronil	20	–	–	–	–	– (0)	–	–	–	–	– (0)
Dieldrin[a]	2	–	–	–	–	– (0)	–	–	–	–	– (0)
p,p′-DDE[b]	2	–	–	–	–	– (0)	–	–	–	–	– (0)
Fipronil sulfone	2	–	–	–	–	– (0)	–	–	–	–	– (0)
Chlorfenapyr	2	–	–	–	–	– (0)	–	–	–	–	– (0)
p,p′-DDD[b]	2	–	–	–	–	– (0)	–	–	–	–	– (0)
p,p′-DDT[b]	20	121.6 ± 64	119	47	201	4(11)	23.1 ± 4	23.1	20	26.26	2 (6)
Bifenthrin	2	3.8 ± 0.5	3.81	3.4	4.22	2(6)	3.69 ± 0.93	4.04	2.1	4.59	5 (14)
Lambda-cyhalothrin	20	–	–	–	–	– (0)	–	–	–	–	– (0)
Overall site detection for all pesticides						2.4					4.1

[a] Banned 1985.
[b] Banned 1972.

samples. Atrazine was the only current-use pesticide that had relatively high concentrations in both sediment and water samples (Tables 3 to 7). In sediment samples, however, atrazine was only above the MDL in 3.1% of all samples (total $n = 261$), but when detected, concentrations were high ($271 \pm 110\ \mu g\ kg^{-1}$) (Table 7). Atrazine was only detected above the MDL in 22% of all water samples analyzed, at concentrations ($13.5 \pm 4\ \mu g\ L^{-1}$) significantly higher than all other current- and past-use pesticides (ANOVA, $F = 6.45$; $P < 0.05$) analyzed (Table 7).

4 DISCUSSION

A study by the USEPA 2001 (Available at http://www.epa.gov/opp00001/pestsales/01pestsales/market_estimates2001.pdf [9 August 2011]) reported that agriculture accounted for 76% of total chemical pesticide use in the United States. The USDA-NASS showed that herbicide usage had increased in 2002 and 2003, specifically in row-crop agriculture of soybeans, corn and cotton. The rise in herbicide use was linked to the increased occurrence of weeds resistant to certain herbicides, increased frequency of and

Table 4. Summary statistics for both water and sediment samples above the minimum detection limit for each respective pesticide analyzed. Beasley and Tallahatchie county site summary statistics are presented herein

		Beasley					Tallahatchie County				
		Overall (μg L^{-1})					Overall (μg L^{-1})				
Pesticide	MDL (μg L^{-1})	Mean ± SD	Median	Min.	Max.	Number of detections (%)	Mean ± SD	Median	Min.	Max.	Number of detections (%)
Water											
Trifluralin	0.02	0.028 ± 0.005	0.031	0.021	0.034	6 (20)	0.035 ± 0.008	0.038	0.025	0.042	3 (19)
Atrazine	1	1.49 ± 0.6	1.288	1.01	2.37	4 (13)	6.49 ± 7.3	3.77	1.4	17	4 (25)
Methyl parathion	2	–	–	–	–	– (0)	–	–	–	–	– (0)
Alachlor	0.1	0.23 ± 0.105	0.225	0.105	0.357	8 (27)	–	–	–	–	– (0)
Metolachlor	0.1	4.64 ± 10.8	0.426	0.2	42.3	15 (50)	1.1 ± 1.69	0.378	0.280	5.511	11 (69)
Chlorpyrifos	0.01	0.019 ± 0.003	0.013	0.01	0.022	8 (27)	0.025 ± 0.004	0.028	0.020	0.029	5 (31)
Cyanazine	0.1	0.103	0.1	0.1	0.1	1 (3)	–	–	–	–	– (0)
Pendimethalin	0.05	0.06 ± 0.01	0.06	0.05	0.07	3 (10)	0.08 ± 0.05	0.088	0.053	0.124	2 (13)
Fipronil	0.2	0.31 ± 0.105	0.318	0.243	0.392	2 (6)	–	–	–	–	– (0)
Dieldrin[a]	0.02	0.026 ± 0.006	0.025	0.021	0.038	6 (20)	0.029	0.02	0.02	0.02	1 (6)
p,p′-DDE[b]	0.02	0.036 ± 0.026	0.026	0.02	0.098	14 (47)	0.03	0.03	0.03	0.03	1 (6)
Fipronil sulfone	0.02	0.035 ± 0.012	0.034	0.02	0.054	16 (53)	0.041 ± 0.02	0.033	0.027	0.074	4 (25)
Chlorfenapyr	0.02	0.058 ± 0.01	0.055	0.02	0.090	12 (40)	0.041 ± 0.02	0.038	0.021	0.081	6 (38)
p,p′-DDD[b]	0.02	0.034 ± 0.019	0.027	0.020	0.104	23 (76)	0.02 ± 0.004	0.021	0.020	0.033	8 (50)
p,p′-DDT[b]	0.2	0.342 ± 0.16	0.253	0.208	0.847	15 (50)	0.314 ± 0.08	0.303	0.236	0.417	4 (25)
Bifenthrin	0.02	0.06 ± 0.055	0.041	0.021	0.189	8 (26)	0.103 ± 0.17	0.143	0.022	0.263	3 (19)
Lambda-cyhalothrin	0.2	–	–	–	–	– (0)	–	–	–	–	– (0)
Overall site detection for all pesticides						27.6					19.1
Sediment											
Trifluralin	2	17.3 ± 16	14.79	2.48	42.5	5 (13)	26.2	26.2	26.2	26.2	1 (4)
Atrazine	100	203 ± 52	203	166	240	2 (6)	–	–	–	–	– (0)
Methyl parathion	200	214	214	214	214	1 (3)	–	–	–	–	– (0)
Alachlor	10	52.8 ± 94	14.1	10.8	245	6 (17)	10.9	10.9	10.9	10.9	1 (4)
Metolachlor	10	118 ± 261	25.4	10.3	815	9 (25)	23.9 ± 10.7	25.7	10.5	41.6	7 (26)
Chlorpyrifos	1	15.6 ± 54	1.58	1.13	248	20 (55)	1.6 ± 0.7	1.36	1.09	3.4	10 (37)
Cyanazine	10	15.3 ± 5.7	13.6	10.7	23	4 (11)	16.2	16.2	16.2	16.2	1 (4)
Pendimethalin	5	8.99 ± 3.2	7.992	5.4	14.9	11 (31)	–	–	–	–	– (0)
Fipronil	20	–	–	–	–	– (0)	–	–	–	–	– (0)
Dieldrin[a]	2	–	–	–	–	– (0)	–	–	–	–	– (0)
p,p′-DDE[b]	2	21.7 ± 35	11.3	3.6	109.7	26 (72)	4.9 ± 4.9	3.422	2.078	22.5	17 (63)
Fipronil sulfone	2	2.48	2.48	2.48	2.48	1 (3)	2.27	2.27	2.27	2.27	1 (4)
Chlorfenapyr	2	3.66 ± 2.88	2.61	2.01	9.1	14 (39)	2.19	2.1	2.1	2.1	1 (4)
p,p′-DDD[b]	2	9.8 ± 10.4	5.9	2.18	41.6	26 (72)	3.07 ± .51	2.326	2	3.4	10 (37)
p,p′-DDT[b]	20	78.5 ± 136	34.4	20.4	582	2 (6)	35 ± 17	26.6	21.3	71.6	8 (30)
Bifenthrin	2	2.53 ± 08	2.53	2.47	2.5	2 (6)	6.04 ± 4.3	6.04	2.9	9.1	2 (7)
Lambda-cyhalothrin	20	–	–	–	–	– (0)	–	–	–	–	– (0)
Overall site detection for all pesticides						25.1					13.6

[a] Banned 1985.
[b] Banned 1972.

concentrated applications of glyphosate and the application of herbicide combinations.[14] Agriculture is the dominant land use in the LMAV because of long growing seasons and conducive climatic conditions (high humidity and rainfall, good soil fertility and flat topography). These ideal growing conditions are also favorable for enhanced weed and insect growth and subsequent high levels of insect/weed control management with selective pesticides.

In Mississippi and Arkansas in 2007, the latest year survey statistics were available, the USDA-NASS website[1] reports soybean herbicide use up 54% and 18%, respectively, from 2004. Across both Arkansas and Mississippi, cotton herbicide and insecticide use was down in 2007 by 18 and 54% and by 46 and 37% respectively. Similarly, USDA-NASS statistics for corn (2001–2005) reported no pesticide use for corn production in Arkansas or

Table 5. Summary statistics for both water and sediment samples above the minimum detection limit for each respective pesticide analyzed. Portageville (water $n = 20$; sediment $n = 27$) and Success (water $n = 33$; sediment $n = 36$) site summary statistics are presented herein

		Portageville					Success				
		Overall ($\mu g\ L^{-1}$)					Overall ($\mu g\ L^{-1}$)				
Pesticide	MDL ($\mu g\ L^{-1}$)	Mean ± SD	Median	Min.	Max.	Number of detections (%)	Mean ± SD	Median	Min.	Max.	Number of detections (%)
Water											
Trifluralin	0.02	0.02 ± 0.001	0.02	0.027	0.028	2 (10)	0.02	0.02	0.02	0.02	1 (3)
Atrazine	1	20.9 ± 18.5	15.4	1.3	58.6	14 (70)	1.4 ± 0.48	1.3	1.03	2.3	10 (32)
Methyl parathion	2	–	–	–	–	– (0)	–	–	–	–	– (0)
Alachlor	0.1	0.36 ± 0.3	0.36	0.12	0.61	2 (10)	0.13 ± 0.025	0.127	0.114	0.163	3 (10)
Metolachlor	0.1	5.4 ± 13	0.88	0.1	49.5	12 (60)	0.88 ± 0.56	1.14	0.23	1.27	3 (10)
Chlorpyrifos	0.01	–	–	–	–	– (0)	0.011 ± 0.0001	0.010	0.010	0.014	4 (13)
Cyanazine	0.1	0.38	0.38	0.38	0.38	1 (5)	0.1	0.1	0.1	0.1	1 (3)
Pendimethalin	0.05	–	–	–	–	– (0)	–	–	–	–	– (0)
Fipronil	0.2	–	–	–	–	– (0)	–	–	–	–	– (0)
Dieldrin[a]	0.02	–	–	–	–	– (0)	–	–	–	–	– (0)
p,p′-DDE[b]	0.02	0.02	0.02	0.02	0.02	1 (5)	–	–	–	–	– (0)
Fipronil sulfone	0.02	0.04 ± 0.015	0.046	0.028	0.06	4 (20)	0.03 ± 0.01	0.022	0.021	0.038	6 (19)
Chlorfenapyr	0.02	0.028 ± 0.008	0.026	0.02	0.047	10 (50)	0.026 ± 0.006	0.025	0.021	0.038	6 (19)
p, p′-DDD[b]	0.02	0.022 ± 0.003	0.021	0.014	0.028	8 (40)	0.025 ± 0.004	0.023	0.020	0.030	8 (26)
p,p′-DDT[b]	0.2	0.45 ± 0.27	0.318	0.226	1.014	10 (50)	0.38 ± 0.15	0.322	0.200	0.691	10(32)
Bifenthrin	0.02	0.03 ± 0.01	0.032	0.024	0.039	3 (15)	0.046 ± 0.02	0.046	0.026	0.067	2 (6)
Lambda-cyhalothrin	0.2	–	–	–	–	– (0)	–	–	–	–	– (0)
Overall site detection for all pesticides						19.7					10.2
Sediment											
Trifluralin	2	18.4 ± 10.2	18.4	11.1	25.7	2 (7)	7.1 ± 6.4	3.9	2.1	21.5	10 (28)
Atrazine	100	372 ± 442	163	128	1035	4 (15)	–	–	–	–	– (0)
Methyl parathion	200	–	–	–	–	– (0)	–	–	–	–	– (0)
Alachlor	10	26.6 ± 6	25.9	19.9	34.5	4 (15)	14.6 ± 5.8	14.6	10.5	18.7	2 (6)
Metolachlor	10	34.4 ± 20	28.6	13.2	82.5	10 (37)	12.7 ± 1.8	12.7	11.4	14	2 (6)
Chlorpyrifos	1	2.76 ± 2.5	1.66	1.05	8.22	14 (52)	–	–	–	–	– (0)
Cyanazine	10	17.8	17.8	17.8	17.8	1 (4)	–	–	–	–	– (0)
Pendimethalin	5	7.6 ± 2.3	6.95	5.7	12	9 (33)	–	–	–	–	– (0)
Fipronil	20	–	–	–	–	– (0)	–	–	–	–	– (0)
Dieldrin[a]	2	–	–	–	–	– (0)	–	–	–	–	– (0)
p,p′-DDE[b]	2	11.7 ± 10.7	7.63	2.11	34	17 (63)	–	–	–	–	– (0)
Fipronil sulfone	2	2.09	2.09	2.09	2.09	1 (4)	–	–	–	–	– (0)
Chlorfenapyr	2	2.91 ± 0.749	2.81	2.13	3.91	4 (15)	–	–	–	–	– (0)
p,p′-DDD[b]	2	5.79 ± 2.9	6.16	2.38	11.6	13 (48)	–	–	–	–	– (0)
p,p′-DDT[b]	20	27.8 ± 6.2	25.8	20.7	38.2	12 (44)	20.2 ± 0.22	20.2	20.1	20.4	2 (6)
Bifenthrin	2	5.4	5.4	5.4	5.4	1 (4)	–	–	–	–	– (0)
Lambda-cyhalothrin	20	–	–	–	–	– (0)	–	–	–	–	– (0)
Overall site detection for all pesticides						21.3					2.7

[a] Banned 1985.
[b] Banned 1972.

Mississippi. Interestingly, a study by Smith *et al.*[7] reported a high percentage of atrazine detection in stream, reservoir water and both stream and reservoir sediments, with atrazine having the highest concentration in storm flow runoff (2.50 $\mu g\ L^{-1}$). This observed concentration is very low compared with the 20.9 $\mu g\ L^{-1}$ water and 372 $\mu g\ kg^{-1}$ sediment concentrations reported in the present study. A 2009 agricultural statistics publication[14] shows that from 2006 to 2008 a doubling in corn production occurred in Mississippi and Arkansas from 137 600 to 291 400 ha and from 77 000 to 178 000 ha respectively. Clark and Goolsby[15] performed a study on pesticide occurrence from 1991 to 1997 in rivers in the Mississippi River Basin and reported atrazine as a frequently detected pesticide (97%). High detection and concentration of atrazine in surface waters is expected, as it is highly soluble (33 $mg\ L^{-1}$), persistent and mobile.[2] Furthermore, atrazine is popular for effective pre-emergent and post-emergent weed control for corn.[16] Atrazine was not frequently detected in this study, with 84% non-detection in sediment samples and only 22% of water samples having detectable concentrations. When detected, however, both water (13 $\mu g\ L^{-1}$) and sediment

Table 6. Summary statistics for both water and sediment samples above the minimum detection limit for each respective pesticide analyzed. Oxford (water $n = 35$; sediment $n = 36$) and Judd Hill (water $n = 8$; sediment $n = 27$) site summary statistics are presented herein

		Oxford					Judd Hill				
		Overall (μg L^{-1})					Overall (μg L^{-1})				
Pesticide	MDL (μg L^{-1})	Mean ± SD	Median	Min.	Max.	Number of detections (%)	Mean ± SD	Median	Min.	Max.	Number of detections (%)
Water											
Trifluralin	0.02	0.171	0.171	0.171	0.171	1 (2.9)	–	–	–	–	– (0)
Atrazine	1	–	–	–	–	– (0)	3.87 ± 3.39	1.186	0.161	10.3	4 (50)
Methyl parathion	2	–	–	–	–	– (0)	–	–	–	–	– (0)
Alachlor	0.1	–	–	–	–	– (0)	–	–	–	–	– (0)
Metolachlor	0.1	0.171	0.171	0.171	0.171	1 (2.9)	0.786 ± 0.807	0.495	0.305	2.224	
Chlorpyrifos	0.01	0.018 ± 0.01	0.014	0.012	0.036	4 (11.4)	0.02 ± 0.005	0.024	0.020	0.028	
Cyanazine	0.1	0.108	0.108	0.108	0.108	1 (2.9)	–	–	–	–	– (0)
Pendimethalin	0.05	0.06	0.06	0.06	0.06	1 (2.9)	–	–	–	–	– (0)
Fipronil	0.2	–	–	–	–	– (0)	–	–	–	–	– (0)
Dieldrin[a]	0.02	0.025 ± 0.005	0.025	0.021	0.029	2 (5.7)	–	–	–	–	– (0)
p,p′-DDE[b]	0.02	0.172 ± 0.28	0.093	0.023	0.8	7 (20)	0.029 ± 0.006	0.028	0.025	0.037	3 (37.5)
Fipronil sulfone	0.02	0.05 ± 0.04	0.036	0.022	0.141	6 (17)	0.03 ± 0.009	0.026	0.021	0.045	4 (50)
Chlorfenapyr	0.02	0.06 ± 0.029	0.059	0.037	0.096	3 (8.5)	0.27	0.27	0.27	0.27	1 (12.5)
p,p′-DDD[b]	0.02	0.077 ± 0.16	0.025	0.02	0.687	14 (40)	0.02 ± 0.007	0.027	0.02	0.04	6 (75)
p,p′-DDT[b]	0.2	0.409 ± 0.15	0.362	0.245	0.605	5 (14)	0.55 ± 0.39	0.339	0.131	1.256	6 (75)
Bifenthrin	0.02	0.147 ± 0.105	0.160	0.036	0.245	3 (8.5)	–	–	–	–	– (0)
Lambda-cyhalothrin	0.2	2.02	2.02	2.02	2.02	1 (2.9)	–	–	–	–	– (0)
Overall site detection for all pesticides						8.2					22.8
Sediment											
Trifluralin	2	2.07	2	2	2	1 (3)	–	–	–	–	– (0)
Atrazine	100	161	161	161	161	1 (3)	110	110	110	110	1 (4)
Methyl parathion	200	–	–	–	–	– (0)	–	–	–	–	– (0)
Alachlor	10	–	–	–	–	– (0)	–	–	–	–	– (0)
Metolachlor	10	61	61	61	61	1 (3)	13.6 ± 6	13.6	13.2	14.1	2 (7)
Chlorpyrifos	1	26.4 ± 48	1.3	1.06	111.6	5 (14)	3.95 ± 6	1.2	1.14	16.2	6 (22)
Cyanazine	10	277 ± 353	277	27.8	528.1	2 (5.5)	–	–	–	–	– (0)
Pendimethalin	5	–	–	–	–	– (0)	–	–	–	–	– (0)
Fipronil	20	–	–	–	–	– (0)	–	–	–	–	– (0)
Dieldrin[a]	2	–	–	–	–	– (0)	–	–	–	–	– (0)
p,p′-DDE[b]	2	4.27 ± 1.6	4.32	2.2	9.08	20 (56)	5.52 ± 6.5	3.5	2.02	23.9	10 (37)
Fipronil sulfone	2	–	–	–	–	– (0)	–	–	–	–	– (0)
Chlorfenapyr	2	–	–	–	–	– (0)	17.3 ± 18	17.3	4.1	30.6	2 (7)
p,p′-DDD[b]	2	2.8 ± 1.4	2.35	2.09	8.4	17 (47)	3.17 ± 1.4	2.7	2.03	6.68	8 (30)
p,p′-DDT[b]	20	24.7 ± 5.1	23.2	20.5	30.4	3 (8)	30.1 ± 6.7	29.4	23.8	37.3	3 (11)
Bifenthrin	2	–	–	–	–	– (0)	7.1 ± 4.5	5.7	2.2	13.1	5 (19)
Lambda-cyhalothrin	20	–	–	–	–	– (0)	–	–	–	–	– (0)
Overall site detection for all pesticides						8.6					8.5

[a] Banned 1985.
[b] Banned 1972.

(271 μg kg^{-1}) concentrations were the highest of all 17 pesticides analyzed. Highest detection percentages and concentrations occurred at sites that were planted in corn (Portageville, MO, and Memphis, TN). Klaine *et al.*[2] reported that only 1.5% of atrazine applied occurred in runoff. However, concentrations as high as 0.25 mg L^{-1} were detected. This correlates well with reported sediment atrazine concentrations in this study (271 μg kg^{-1}). Klaine *et al.*[2] also described atrazine in soils and reported first-order decay trends, with only 1.88% of the initial concentration remaining 238 days post-application. Atrazine has also been found in groundwater beneath irrigated agriculture in Nebraska at 88 μg L^{-1}, much higher than encountered during this study.[2]

There were pesticides analyzed that had very few detections. The lack of detection (0 and 0.5% of samples above the detection limit) of methyl-parathion, an insecticide typically used for stink-bug (Pentatomidae) control in cotton, is not surprising because the majority of ditches surveyed were cropped in soybeans, corn or rice (with Oxford the exception for cotton). Furthermore, the prevalence of corn superseding cotton in agriculture for ethanol

Table 7. Percentage detection above lower limit detection and average concentrations when detected for 17 pesticides in water and sediment samples from the LMAV

Pesticide	Minimum detection limits ($\mu g\ L^{-1}$) water	Minimum detection limits ($\mu g\ kg^{-1}$) sediment	% Non-detection		% Above lower limit of detection		Average concentration detected	
			Water	Sediment	Water	Sediment	Water ($\mu g\ L^{-1}$)	Sediment ($\mu g\ kg^{-1}$)
Trifluralin	0.02	2	54.3	63.2	10.0	8.4	0.04	10.5
Atrazine	1	100	33.3	84.3	22.4	3.1	13.5	271.3
Methyl parathion	2	200	45.7	69.3	<actual MDL	0.5	<actual MDL	214.3*
Alachlor	0.1	10	26.2	53.6	7.6	6.1	0.2	31.4
Metolachlor	0.1	10	35.2	59.8	30.0	13.4	4.1	50.2
Chlorpyrifos	0.01	1	61.4	57.5	10.0	24.9	0.02	8.4
Cyanazine	0.1	10	51.4	73.6	3.3	3.8	0.2	67.6
Pendimethalin	0.05	5	44.3	49.8	4.3	8.4	0.1	8.2
Fipronil	0.2	20	0.5	29.1	1.9	<actual MDL	0.4	<actual MDL
Dieldrin[a]	0.02	2	0.9	11.1	7.1	1.9	0.03	3.9
p,p′-DDE[b]	0.02	2	8.1	20.3	14.3	34.5	0.1	11.1
Fipronil sulfone	0.02	2	<actual MDL	9.9	27.1	1.5	0.04	2.2
Chlorfenapyr	0.02	2	3.3	22.9	24.8	8.1	0.05	4.8
p,p′-DDD[b]	0.02	2	0.5	17.6	35.7	28.4	0.04	5.9
p,p′-DDT[b]	0.2	20	0.5	0.3	33.8	19.9	0.4	53.2
Bifenthrin	0.02	2	50.9	46.4	11.0	6.5	0.1	4.9
Lambda-cyhalothrin	0.2	20	51.4	81.2	26.2	<actual MDL	0.1	<actual MDL
Overall average			27.5	44.1	15.9	10.0	1.1	43.9
Overall SE			5.7	6.3	2.9	2.6	0.3	13.1

[a] Banned 1985.
[b] Banned 1972.
* Only value above lower limit of detection.

production has reduced cotton farming to very low acreage. There were similar low detection levels for other pesticides associated with cotton: herbicides trifluralin and pendimethalin (<10% detection), as well as insecticides lambda-cyhalothrin, bifenthrin and chlorofenapyr (>30%). Few detections and very low concentrations of pendimethalin (Table 3) support findings by Stahnke *et al.*[17] that only trace levels (<0.003 mg kg^{-1}) of pendimethalin were observed in drainage waters and sediments, with very little leaching from initial application.

Dieldrin, *p,p′*-DDT and its metabolites DDE and DDD are past-use organochlorine pesticides that were banned and discontinued in the early 1970s. In examining water and sediment samples, Smith *et al.*[7] reported a high number of detections of *p,p′*-DDT, the most detections of all current- and past-use and metabolites of current- and past-use pesticides examined. This result was surprising, as the use of such pesticides was banned over 30 years ago. In summation, Smith *et al.*[7] highlighted that dieldrin, *p,p′*-DDT, DDE and DDD accounted for 34% of all pesticide detections in a study over 4 years. In the present study, dieldrin was detected <8% of the time in water and <2% of the time in all sediment samples analyzed, while *p,p′*-DDT and metabolites DDD and DDE were above the MDL in <36% of water and sediment samples, which is very similar to the findings of Smith *et al.*[7] Although these were the highest detection percentages of all pesticides analyzed, concurring with the values obtained by Smith *et al.*,[7] the average concentrations of the pesticides were very low in water (0.4, 0.04 and 0.1 $\mu g\ L^{-1}$ respectively), and only an average of 0.2 $\mu g\ L^{-1}$ above the analytical instrument detection limit. Median sediment concentration for DDT when detected (20%) were 53 $\mu g\ kg^{-1}$. Smith *et al.*[7] did not report *p,p′*-DDT concentrations when detected, and thus the potential differences in observed values cannot be compared.

5 CONCLUSIONS

Agricultural drainage ditch waters and sediments in the LMAV had generally low current-use and past-use pesticide and metabolite concentrations, and a high percentage of samples with non-detectable concentrations. In spite of the historical context of pesticide use in agriculture and the history of agriculture in the Mississippi Delta, drainage systems have very low measured pesticide concentrations. Studies that increase the number of sample sites as well as sampling frequency and duration, in conjunction with these results, will provide data that can be used for understanding the contributions of pesticide concentrations to downstream aquatic systems.

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REFERENCES

1 *USDA National Statistics Service.* [Online]. USDA-NASS. Available: http://www.nass.usda.gov/Publications/Ag_Statistics/2009/chp14.pdf [30 June 2010].

2 Klaine SF, Hinman ML, Winkelmann DA, Sauser KR, Martin JR and Moore LW, Characterization of agricultural nonpoint pollution: pesticide migration in a west Tennessee watershed. *Environ Toxicol Chem* **7**:609–614 (1988).
3 Ridgway RL, Tinney JC, MacGregor JT and Starler NJ, Pesticide use in agriculture. *Environ Health Perspectives* **27**:103–112 (1978).
4 Kiely T, Donaldson D and Grube A, Pesticides industry sales and usage: 2000 and 2001 market estimates. USEPA Office of Prevention, Pesticides, and Toxic Substances (7503C), EPA-733-R-04-001 (2004).
5 Pimental D, Acquay H, Biltonen M, Rice P, Silva M, Nelson J, *et al*, Assessment of environmental and economic costs of pesticide use, in *Pesticide Question: Environment, Economics and Ethics*, ed. by Pimental D and Lehman H. Chapman and Hall, New York, NY, pp. 47–84 (1993).
6 Cooper CM, Smith SJ and Moore MT, Surface water, ground water and sediment quality in three oxbow lake watersheds in the Mississippi Delta agricultural region: pesticides. *Int J Ecol Env Sci* **29**:171–184 (2003).
7 Smith S, Jr, Cooper CM, Lizotte RE, Jr., and Shields FD, Jr, Storm pesticide concentrations in Little Topashaw Creek, USA. *Int J Ecol Environ Sci* **32**:173–182 (2006).
8 Smith SJ and Cooper CM, Pesticides in shallow groundwater and lake water in the Mississippi Delta MSEA, in *Water Quality Assessments in the Mississippi Delta, Regional Solutions, National Scope*, ed. by Nett M, Locke M and Pennington D. *ACS Symposium Series* 877, American Chemical Society, Oxford University Press, Chicago, IL, pp. 91–103 (2004).
9 Cooper CM, Moore MT, Bennett ER, Smith SJ, Farris JL, Milam CD, *et al*, Innovative uses of vegetated drainage ditches for reducing agricultural runoff. *Water Sci Technol* **49**:117–123 (2004).
10 Moore MT, Bennett ER, Cooper CM, Smith SJ, Shields FD, Jr, Milam CD, *et al*, Transport and fate of atrazine and lambda-cyhalothrin in an agricultural drainage ditch in the Mississippi Delta, USA. *Agr Ecosyst Environ* **87**:309–314 (2001).
11 Bennett ER, Moore MT, Cooper CM and Smith SJ, Method for simultaneous extraction and analysis of two current use pesticides, atrazine and lambda-cyhalothrin, in sediment and aquatic plants. *B Environ Contam Tox* **64**:825–833 (2000).
12 *JMP Version 5.0.1*. SAS Institute, Cary, NC (2002).
13 *Extoxnet, The Extension Toxicology Network*. [Online]. National Pesticide Information Center, Oregon State University. Available: http://extoxnet.orst.edu/ [10 October 2010].
14 *USDA National Statistics Service*. [Online]. USDA-NASS. Available: http://www.nass.usda.gov/Publications/Ag_Statistics/2009/chp01.pdf [15 September 2010].
15 Clark GM and Goolsby DA, Discharge of herbicides from the Mississippi River Basin to the Gulf of Mexico, 1991–1997. US Geological Survey, USGS Fact Sheet FS-163-98 (1999).
16 Hyer KE, Hornberger GM and Herman JS, Processes controlling episodic streamwater transport of atrazine and other agrichemicals in an agricultural watershed. *J Hydrol* **254**:47–66 (2001).
17 Stahnke GK, Shea PJ, Tupy DR, Stougaard RN and Shearman RC, Pendimethalin dissipation in Kentucky Bluegras turf. *Weed Sci* **39**:97–103 (1991).

